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Process and apparatus for the continuous production of a thermoplastic polymer blend and use thereof

5 This invention relates to a process and an apparatus for the production of a thermoplastic polymer blend from polycarbonate, a thermoplastic polyester and/or vinyl polymers, optionally together with further additives and to the use of such a polymer blend.

10 The production of thermoplastic polymer blends is known from the most varied embodiments. Production proceeds by melting and subsequent mixing of the blend components using, for example, screw compounders or kneaders (for example compounding by means of extruders or injection moulding machines). The starting thermoplastics of the blend assume the form of solids, for example pellets or powders, before they are melted. Further additives are frequently also added in addition to the  
15 thermoplastic blend components during the mixing step. WO 92/19676 accordingly describes a process for the production of a polymer blend, wherein two polymers to be mixed are initially melted and the two polymer streams are then mixed together. In this known blend production method, a continuous, fibrous morphology is formed during mixing which reinforces the polymer blend. The polymer which is capable of  
20 forming said fibres originates from the range of liquid crystalline thermoplastics (LCP). Another process is described in US-A 4,547,541. In this case, too, two different polymers are initially melted separately and the two polymer melt streams are adjusted to a certain temperature, in order to achieve optimum mixing while retaining desired properties.

EP-A 0 340 655 furthermore discloses a process in which thermally incompatible polymers may be mixed together. In this case, too, the individual polymer streams are initially adjusted to a predetermined temperature in separate extruders, in order subsequently to be mixed. Polymers are defined as thermally incompatible if the thermal processing windows thereof are separated by a temperature difference of greater than 5°C.

Accordingly, in the prior art, the thermoplastics from which the polymer blend is produced are supplied in solid form to the site at which the blend is produced. Production of the thermoplastics prior to said supply (primary production) generally occurs remotely from the blend production site and proceeds by chemically linking monomeric structural units (for example by polymerisation, polycondensation, polyaddition). Supplying the thermoplastics to the blend production site in solid form presupposes that the thermoplastics solidify in the primary production plant by cooling and are then optionally pelletised. This general, conventional approach entails the following disadvantages:

The stated steps of cooling, solidification, pelletisation, storage, transport and melting are costly and logistically complex. Moreover, the requisite energy consumption results in environmental impact. Melting the blend components in the compounding facility constitutes additional exposure of the thermoplastics to elevated temperatures, which may result in degradation and thus poorer blend characteristics. This applies in particular to heat-sensitive polymers. Finally, it may prove necessary to dry the thermoplastics used at the blend production site before they are melted, if any moisture absorbed during transport and storage would result in polymer degradation of the thermoplastics in the melt. Moreover, the above-stated known processes for the production of a thermoplastic polymer blend entail complex plants, as, once melted, the individual product streams must first be adjusted to a certain temperature level so that they may be mixed with each other in an optimal manner.

The object of the invention is accordingly to provide a process and apparatus for the production of a thermoplastic polymer blend of polycarbonate and at least one thermoplastic polyester and/or elastomeric polymer, optionally together with further additives, in which it is possible to dispense with the described solidification, pelletisation, transport, drying and melting steps for at least one thermoplastic.

This object is achieved according to the process by the following steps:

- drawing at least one of the thermoplastics used for the production of the polymer blend, preferably polycarbonate or polybutylene terephthalate, particularly preferably aromatic polycarbonate, in the molten state directly from primary production,
- optionally melting the blend components which are to be incorporated,
- adding the blend components which are to be incorporated into the thermoplastic melt drawn from primary production,
- mixing all the components in a mixing section and
- cooling and optionally pelletising the polymer melt.

The polymer melt produced according to the invention is in particular suitable for the production of semi-finished products, such as for example films, solid sheets, twin-wall sheets, profiles or tubes.

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In the preferred case of drawing polycarbonate from primary production, the object is achieved in terms of apparatus by means of a plant substantially consisting of a tubular evaporator arranged in a first separator, a strand evaporator arranged in a second separator, at least one extruder for melting the blend components, at least one mixer, preferably a static mixer, and optionally an apparatus for pelletising the polymer blend, wherein the individual components are interconnected by piping.

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In a further development of the invention, molten polycarbonate is used from primary production, wherein the temperature of the polycarbonate prior to addition of the blend components which are to be incorporated is 220 to 320°C, preferably 270 to 300°C, particularly preferably 280 to 290°C.

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Since in many production processes the temperature of the polycarbonate melt is up to 350°C, it is not possible to admix heat-sensitive blend components at this temperature without damaging the blend components which are to be incorporated. However, in the apparatus according to the invention, the structure of which is described in greater

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detail below, it is possible to mix the molten blend components directly into the polycarbonate melt. This results in a distinct improvement to the process since it is possible to dispense with the steps described above (solidification, pelletisation, storage, transport, drying, melting) and the corresponding temperature-control components, such that, on the one hand, plant and equipment costs, including those for control systems, and, on the other, the physical size of the plant and thus the cost thereof, may be minimised. Environmental impact may also be reduced. Finally, it is possible, without any modification of temperature, to use a conventional plant to produce the polycarbonate and also to produce the desired polymer blend of polycarbonate and at least one blend component.

In an alternative development of the invention, the thermoplastic which is drawn from primary production in a molten state is a thermoplastic polyester, preferably polybutylene terephthalate, polytrimethylene terephthalate or polyethylene terephthalate, particularly preferably polybutylene terephthalate. On addition of the other blend components, the temperature of the polybutylene terephthalate melt is 220 to 320°C, preferably 230 to 300°C, particularly preferably 240 to 280°C.

A polymer blend which is preferably to be produced contains

- A: 2 to 98 parts by weight of thermoplastic polyester, preferably in total 10 to 60 parts by weight of polybutylene terephthalate, polytrimethylene terephthalate and/or polyethylene terephthalate, particularly preferably 10 to 60 parts by weight of polybutylene terephthalate, in particular preferably 30 to 50 parts by weight of polybutylene terephthalate
- B: 2 to 98 parts by weight of aromatic polycarbonate, preferably 40 to 90 parts by weight of aromatic polycarbonate,
- C: 0 to 30 parts by weight of graft polymer, preferably 4 to 25 parts by weight of graft polymer,

- 5 -

- D: 0 to 25 parts by weight of additives, preferably 0.05 to 20 parts by weight of additives, particularly preferably 0.1 to 10 parts by weight of additives, wherein the sum of all parts by weight of components A-D is 100.

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Another polymer blend which is preferably to be produced contains

- A: 2 to 98 parts by weight of thermoplastic polyester, preferably in total 10 to 60 parts by weight of polybutylene terephthalate, polytrimethylene terephthalate and/or polyethylene terephthalate, particularly preferably 10 to 60 parts by weight of polybutylene terephthalate, in particular preferably 30 to 50 parts by weight of polybutylene terephthalate
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- B: 2 to 98 parts by weight of aromatic polycarbonate, preferably 40 to 90 parts by weight of aromatic polycarbonate,
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- C: 0 to 30 parts by weight of graft polymer, preferably 4 to 25 parts by weight of graft polymer,
- D: 0 to 30 parts by weight of thermoplastic vinyl copolymer, preferably 4 to 25 parts by weight of thermoplastic vinyl copolymer,
- 20
- E: 0 to 25 parts by weight of additives, preferably 0.05 to 20 parts by weight of additives, particularly preferably 0.1 to 10 parts by weight of additives, wherein the sum of all parts by weight of components A-E is 100.
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Another polymer blend which is preferably to be produced contains:

- A: 40 to 99 parts by weight of aromatic polycarbonate, preferably 60 to 98 parts by weight of aromatic polycarbonate,
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- B: 0 to 60 parts by weight of graft polymer, preferably 1 to 40 parts by weight of graft polymer, particularly preferably 2 to 25 parts by weight of graft polymer
- 5 C: 0 to 45 parts by weight of thermoplastic vinyl copolymer, preferably 0 to 30 parts by weight of thermoplastic vinyl copolymer, particularly preferably 2 to 25 parts by weight of thermoplastic vinyl copolymer,
- 10 D: 0 to 30 parts by weight of additives, preferably 0.05 to 25 parts by weight of additives, particularly preferably 0.1 to 17 parts by weight of additives, wherein the sum of all parts by weight of components A-D is 100.

Aromatic polycarbonates are described below:

15 According to the invention, any polycarbonate may be used. Polycarbonates which are suitable according to the invention are both homopolycarbonates and copolycarbonates. A mixture of polycarbonates suitable according to the invention may also be used. The polycarbonates may be partially or entirely replaced by aromatic polyester carbonates.

20 Preferred polycarbonates are those homopolycarbonates and copolycarbonates based on bisphenols of the general formula (I)



25 in which

Z is a divalent organic residue having 6 to 30 C atoms, which contains one or more aromatic groups.

30 Examples of bisphenols of the general formula (I) are bisphenols belonging to the following groups:

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dihydroxydiphenyls,  
bis(hydroxyphenyl)alkanes,  
bis(hydroxyphenyl)cycloalkanes,  
indanebisphenols,  
5 bis(hydroxyphenyl) sulfides,  
bis(hydroxyphenyl) ethers,  
bis(hydroxyphenyl) ketones,  
bis(hydroxyphenyl) sulfones,  
bis(hydroxyphenyl) sulfoxides and  
10  $\alpha,\alpha'$ -bis(hydroxyphenyl)diisopropylbenzenes.

Derivatives of the stated bisphenols, which may for example be obtained by alkylation or halogenation on the aromatic rings of the stated bisphenols, are also examples of bisphenols according to the general formula (I).

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Examples of bisphenols according to the general formula (I) are in particular the following compounds: -

hydroquinone,  
resorcinol,  
20 4,4'-dihydroxydiphenyl,  
bis(4-hydroxyphenyl) sulfide,  
bis(4-hydroxyphenyl) sulfone,  
bis(3,5-dimethyl-4-hydroxyphenyl)methane,  
bis(3,5-dimethyl-4-hydroxyphenyl) sulfone,  
25 1,1-bis(3,5-dimethyl-4-hydroxyphenyl)-p/m-diisopropylbenzene,  
1,1-bis(4-hydroxyphenyl)-1-phenylethane,  
1,1-bis(3,5-dimethyl-4-hydroxyphenyl)cyclohexane,  
1,1-bis(4-hydroxyphenyl)-3-methylcyclohexane,  
1,1-bis(4-hydroxyphenyl)-3,3-dimethylcyclohexane,  
30 1,1-bis(4-hydroxyphenyl)-4-methylcyclohexane,  
1,1-bis(4-hydroxyphenyl)cyclohexane,

- 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane,  
2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane,  
2,2-bis(3-methyl-4-hydroxyphenyl)propane,  
2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane,  
5 2,2-bis(4-hydroxyphenyl)propane (*i.e.* bisphenol A),  
2,2-bis(3-chloro-4-hydroxyphenyl)propane,  
2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane,  
2,4-bis(4-hydroxyphenyl)-2-methylbutane,  
2,4-bis(3,5-dimethyl-4-hydroxyphenyl)-2-methylbutane,  
10  $\alpha,\alpha'$ -bis(4-hydroxyphenyl)-o-diisopropylbenzene,  
 $\alpha,\alpha'$ -bis(4-hydroxyphenyl)-m-diisopropylbenzene (*i.e.* bisphenol M),  
 $\alpha,\alpha'$ -bis(4-hydroxyphenyl)-p-diisopropylbenzene and  
indanebisphenol.
- 15 Particularly preferred polycarbonates are the homopolycarbonate based on bisphenol A, the homopolycarbonate based on 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane and the copolycarbonates based on the two monomers bisphenol A and 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane.
- 20 The described bisphenols according to the general formula (I) may be produced using known processes, for example from the corresponding phenols and ketones.
- The stated bisphenols and processes for the production thereof are described, for example, in the monograph by H. Schnell, *Chemistry & Physics of Polycarbonates*,  
25 *Polymer Reviews*, volume 9, pages 77-98, Interscience Publishers, New York, London, Sydney, 1964 and in US-A 3 028 635, in US-A 3 062 781, in US-A 2 999 835, in US-A 3 148 172, in US-A 2 991 273, in US-A 3 271 367, in US-A 4 982 014, in US-A 2 999 846, in DE-A 1 570 703, in DE-A 2 063 050, in DE-A 2 036 052, in DE-A 2 211 956, in DE-A 3 832 396 and in FR-A 1 561 518 and in the  
30 Japanese published patent applications with the application numbers 62039/1986, 62040/1986 and 105550/1986.



1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane and the production thereof is described, for example, in US-A 4 982 014.

5 Indanebisphenols and the production thereof are described, for example, in US-A 3 288 864, in JP-A 60 035 150 and in US-A 4 334 106. Indanebisphenols may, for example, be produced from isopropenylphenol or the derivatives thereof or from dimers of isopropenylphenol or the derivatives thereof in the presence of a Friedel-Crafts catalyst in organic solvents.

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Polycarbonates may be produced using known processes. Suitable processes for the production of polycarbonates are, for example, production from bisphenols with phosgene using the phase interface process or from bisphenols with phosgene using the homogeneous phase process, the so-called pyridine process, or from bisphenols  
15 with carbonic acid esters using the melt transesterification process. These production processes are described, for example, in H. Schnell, *Chemistry & Physics of Polycarbonates, Polymer Reviews*, volume 9, pages 31-76, Interscience Publishers, New York, London, Sydney, 1964. The stated production processes are also described in D. Freitag, U. Grigo, P.R. Müller, N. Nouvertne, *Polycarbonates in Encyclopedia of Polymer Science & Engineering*, volume 11, 2<sup>nd</sup> edition, 1988, pp. 648-718 and in  
20 U. Grigo, K. Kircher and P.R. Müller, *Polycarbonates in Becker/Braun, Kunststoff-Handbuch*, volume 3/1, *Polycarbonate, Polyacetale, Polyester, Celluloseester*, Carl Hanser Verlag, Munich/Vienna, 1992, pages 117-299 and in D.C. Prevorsek, B.T. Debona and Y. Kesten, Corporate Research Center, Allied Chemical Corporation,  
25 Morristown, New Jersey 07960, *Synthesis of Poly(estercarbonate) Copolymers in Journal of Polymer Science, Polymer Chemistry Edition*, volume 19, 75-90 (1980).

The melt transesterification process is in particular described in H. Schnell, *Chemistry & Physics of Polycarbonates, Polymer Reviews*, volume 9, pages 44-51, Interscience  
30 Publishers, New York, London, Sydney, 1964 and in DE-A 1 031 512, in US-A 3 022 272, in US-A 5 340 905 and in US-A 5 399 659.

The raw materials and auxiliaries used in the production of polycarbonates preferably have a low content of impurities. Especially when production is performed using the melt transesterification process, the bisphenols and carbonic acid derivatives used should have the lowest possible content of alkali metal ions and alkaline earth metal ions. Raw materials of such purity are obtainable, for example, by recrystallising, washing or distilling the carbonic acid derivatives, for example carbonic acid esters, and the bisphenols.

When producing polycarbonates by the melt transesterification process, the bisphenol and carbonic acid diester may be reacted continuously or discontinuously, for example in stirred tank reactors, film evaporators, falling-film evaporators, stirred tank reactors connected in series, extruders, kneaders, simple disk reactors and high viscosity disk reactors.

Carbonic acid diesters which may be used for the production of polycarbonates are, for example, diaryl esters of carbonic acid, wherein both aryl residues preferably each have 6 to 14 C atoms. The diesters of carbonic acid based on phenol or alkyl-substituted phenols, thus for example diphenyl carbonate or dicresyl carbonate, are preferably used. Relative to 1 mol of bisphenol, the carbonic acid diesters are preferably used in a quantity of 1.01 to 1.30 mol, particularly preferably in a quantity of 1.02 to 1.15 mol.

The polycarbonates suitable according to the invention preferably have a weight average molar mass ( $\overline{M}_w$ ), which may for example be determined by ultracentrifugation or measurement of light scattering, of 10000 to 200000 g/mol. They particularly preferably have a weight average molar mass of 12000 to 80000 g/mol.

The average molar mass of the polycarbonates according to the invention may, for example, be adjusted in known manner by a suitable quantity of chain terminators.

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The chain terminators may be used individually or as a mixture of various chain terminators.

Suitable chain terminators are both monophenols and monocarboxylic acids. Suitable monophenols are, for example, phenol, p-chlorophenol, p-tert.-butylphenol, cumylphenol or 2,4,6-tribromophenol, as well as long-chain alkylphenols, such as for example 4-(1,1,3,3-tetramethylbutyl)phenol or monoalkylphenols or dialkylphenols having a total of 8 to 20 C atoms in the alkyl substituents, such as for example 3,5-di-tert.-butylphenol, p-tert.-octylphenol, p-dodecylphenol, 2-(3,5-dimethylheptyl)phenol or 4-(3,5-dimethylheptyl)phenol. Suitable monocarboxylic acids are benzoic acid, alkylbenzoic acids and halobenzoic acids.

Preferred chain terminators are phenol, p-tert.-butylphenol, 4-(1,1,3,3-tetramethylbutyl)phenol and cumylphenol.

The quantity of chain terminators is preferably between 0.25 and 10 mol%, relative to the sum of bisphenols used in the particular case.

Polycarbonates suitable according to the invention may be branched in known manner, namely preferably by incorporating trifunctional or greater than trifunctional branching agents. Suitable branching agents are, for example, those having three or more than three phenolic groups or those having three or more than three carboxylic acid groups.

Suitable branching agents are, for example, phloroglucinol, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-2-heptene, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)heptane, 1,3,5-tri-(4-hydroxyphenyl)benzene, 1,1,1-tris(4-hydroxyphenyl)ethane, tri-(4-hydroxyphenyl)phenylmethane, 2,2-bis[4,4-bis(4-hydroxyphenyl)cyclohexyl]propane, 2,4-bis(4-hydroxyphenylisopropyl)phenol, 2,6-bis(2-hydroxy-5'-methylbenzyl)-4-methylphenol, 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)propane, hexa-(4-(4-hydroxyphenylisopropyl)phenyl)terephthalic acid ester, tetra-(4-hydroxyphenyl)-

methane, tetra-(4-(4-hydroxyphenylisopropyl)phenoxy)methane and 1,4-bis(4',4"-dihydroxytriphenyl)methylbenzene together with 2,4-dihydroxybenzoic acid, trimesic acid, cyanuric chloride, 3,3-bis(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindole, trimesic acid trichloride and  $\alpha,\alpha'\alpha''$ -tris(4-hydroxyphenol)-1,3,5-triisopropylbenzene.

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Preferred branching agents are 1,1,1-tris(4-hydroxyphenyl)ethane and 3,3-bis(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindole.

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The quantity of the optional branching agents to be used is preferably 0.05 mol% to 2 mol%, relative to the number of moles of bisphenols used.

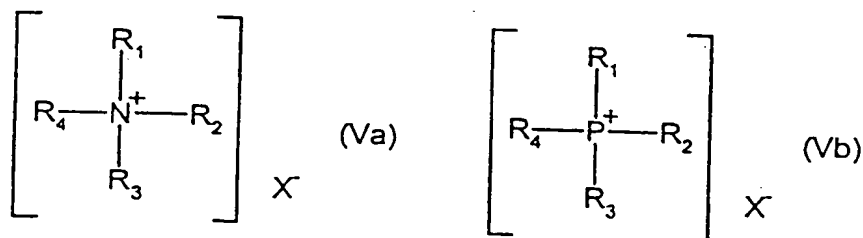
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For example, when producing the polycarbonate using the phase interface process, the branching agents may be initially introduced with the bisphenols and the chain terminators in the alkaline aqueous phase, or may be added dissolved in an organic solvent together with the carbonic acid derivatives. In the case of the transesterification process, the branching agents are preferably apportioned together with the dihydroxyaromatics or bisphenols.

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Catalysts which are preferably to be used in the production of polycarbonate using the melt transesterification process are the ammonium salts and phosphonium salts known from the literature (*c.f.* for example US-A 3 442 864, JP-A-14742/72, US-A 5 399 659 and DE-A 19 539 290).

Examples of such compounds are represented by the general formulae (Va) and (Vb):



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in which

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$R_1$  to  $R_4$  may mutually independently be  $C_1$ - $C_{16}$  alkyls/aryls or cycloalkyls and  $X^-$  is an anion, for which the corresponding acid/base pair  $H^+ + X^- \rightleftharpoons HX$  has a  $pK_b$  value of less than 11.

5      Suitable ammonium salts or phosphonium salts are, for example,

tetramethylammoniumtetraphenyl hydridoborate,  
tetraphenylphosphonium phenolate,  
tetraphenylphosphonium fluoride,  
10      tetraphenylphosphoniumtetraphenyl hydridoborate,  
dimethyldiphenylammonium hydroxide,  
tetraethylammonium hydroxide,  
tetramethylammonium hydroxide,  
tetramethylammonium acetate and  
15      tetramethylammonium fluoride.

Further preferably used catalysts are guanidines according to US-A 5 319 066, but imidazoles are also suitable.

20      The catalysts are preferably used in quantities of  $10^{-8}$  to  $10^{-4}$  mol, particularly preferably in a concentration of  $10^{-7}$  to  $10^{-5}$  mol, relative to 1 mol of bisphenol.

The catalysts may be used alone or in combination with each other; they may be added at the beginning of the process or not until the process is under way.

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Where catalyst combinations are used, alkali metal or alkaline earth metal compounds or salts may also be used, specifically during the course of the process, *i.e.* during the polycondensation phase, as is explained in US-A 5 399 659, which has already been cited above.

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Thermoplastic polyesters are described below: Polyalkylene terephthalates are preferably used as the thermoplastic polyesters. The polyalkylene terephthalates are reaction products prepared from aromatic dicarboxylic acids or the reactive derivatives thereof, such as dimethyl esters or anhydrides, and aliphatic, cycloaliphatic or araliphatic diols, as well as mixtures of these reaction products.

Preferred polyalkylene terephthalates contain at least 80 wt.%, preferably at least 90 wt.%, relative to the dicarboxylic acid component, of terephthalic acid residues and 80 wt.%, preferably at least 90 mol%, relative to the diol component, of ethylene glycol, 1,4-butanediol, and/or 1,3-propanediol residues.

Preferred polyalkylene terephthalates may contain, apart from terephthalic acid residues, up to 20 mol%, preferably up to 10 mol%, of residues of other aromatic or cycloaliphatic dicarboxylic acids having 8 to 14 C atoms or aliphatic dicarboxylic acids having 4 to 12 C atoms, such as for example residues of phthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, 4,4'-diphenyldicarboxylic acid, succinic acid, adipic acid, sebacic acid, azelaic acid, cyclohexanediadic acid.

Preferred polyalkylene terephthalates may contain, apart from ethylene glycol, 1,3-propanediol or 1,4-butanediol residues, up to 20 mol%, preferably up to 10 mol%, of other aliphatic diols having 3 to 12 C atoms or cycloaliphatic diols having 6 to 21 C atoms, for example residues of 1,3-propanediol, 2-ethyl-1,3-propanediol, neopentyl glycol, 1,5-pentanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, 3-ethyl-2,4-pentanediol, 2-methyl-2,4-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, 2-ethyl-1,3-hexanediol, 2,2-diethyl-1,3-propanediol, 2,5-hexanediol, 1,4-di-( $\beta$ -hydroxyethoxy)-benzene, 2,2-bis(4-hydroxycyclohexyl)propane, 2,4-dihydroxy-1,1,3,3-tetramethylcyclobutane, 2,2-bis(4- $\beta$ -hydroxyethoxyphenyl)propane and 2,2-bis(4-hydroxypropoxyphenyl)propane (DE-OS 2 407 674, 2 407 776, 2 715 932).

The polyalkylene terephthalates may be branched by incorporating relatively small quantities of tri- or tetrahydric alcohols or tri- or tetrabasic carboxylic acids, for

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example according to DE-OS 1 900 270 and US patent 3 692 744. Examples of preferred branching agents are trimesic acid, trimellitic acid, trimethylolethane, trimethylolpropane and pentaerythritol.

5 Particularly preferred polyalkylene terephthalates are those which have been produced solely from terephthalic acid and the reactive derivatives thereof (for example the dialkyl esters thereof) and ethylene glycol, 1,3-propanediol and/or 1,4-butanediol, and mixtures of these polyalkylene terephthalates. Polybutylene terephthalate, polytrimethylene terephthalate and polyethylene terephthalate and mixtures of these  
10 polyalkylene terephthalates are particularly preferred. Polybutylene terephthalate is very particularly preferred.

Preferably, mixtures of polyalkylene terephthalates contain 1 to 50 wt.%, preferably 1 to 30 wt.%, of polyethylene terephthalate and 50 to 99 wt.%, preferably 70 to  
15 99 wt.%, of polybutylene terephthalate.

Preferably used polyalkylene terephthalates generally have an intrinsic viscosity of 0.4 to 1.5 dl/g, preferably of 0.5 to 1.2 dl/g, measured in phenol/o-dichlorobenzene (1:1 parts by weight) at 25°C in a Ubbelohde viscosimeter.  
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The polyalkylene terephthalates may be produced using known methods (*c.f.* for example *Kunststoff-Handbuch*, volume VIII, pages 695 *et seq.*, Carl-Hanser Verlag, Munich 1973).

25 Graft polymers and thermoplastic vinyl copolymers together constitute the group of vinyl polymers.

Graft polymers are described below: These include graft copolymers having rubber-elastic properties, which are substantially available from at least 2 of the following  
30 monomers: chloroprene, 1,3-butadiene, isoprene, styrene, acrylonitrile, ethylene, propylene, vinyl acetate and (meth)acrylic acid esters having 1 to 18 C atoms in the

alcohol component; *i.e.* polymers as are described in *Methoden der Organischen Chemie* (Houben-Weyl), volume 14/1, Georg Thieme Verlag, Stuttgart, 1961, pages 393-406 and in C.B. Bucknall, *Toughened Plastics*, Appl. Science Publishers, London 1977. Preferred polymers C are partially crosslinked and have gel contents of above  
5 20 wt.%, preferably of above 40 wt.%, in particular of above 60 wt.%.

Preferred graft polymers C comprise graft polymers prepared from:

- 10 C.1 5 to 95, preferably 30 to 80 parts by weight of a mixture of
- C.1.1 50 to 99 parts by weight of styrene,  $\alpha$ -methylstyrene, halogen or methyl ring-substituted styrenes, methyl methacrylate or mixtures of these compounds and
- 15 C.1.2 1 to 50 parts by weight of acrylonitrile, methacrylonitrile, methyl methacrylate, maleic anhydride, C<sub>1</sub>-C<sub>4</sub> alkyl- or phenyl-N-substituted maleimides or mixtures of these compounds on
- 20 C.2 5 to 95, preferably 20 to 70 parts by weight of diene and/or alkyl acrylate based polymer having a glass transition temperature of below -10°C.

Preferred graft polymers C are, for example, backbones C.2, such as polybutadienes, butadiene/styrene copolymers and acrylate rubbers, grafted with styrene and/or acrylonitrile and/or (meth)acrylic acid alkyl esters; *i.e.* copolymers of the type  
25 described in DE-OS 1 694 173 (= US patent 3 564 077); polybutadienes, butadiene/styrene or butadiene/acrylonitrile copolymers, polyisobutenes or polyisoprenes grafted with acrylic or methacrylic acid alkyl esters, vinyl acetate, acrylonitrile, styrene and/or alkylstyrenes, as are described, for example, in DE-OS 2 348 377 (= US patent 3 919 353).



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Particularly preferred polymers C are, for example, ABS polymers, as are for example described in DE-OS 2 035 390 (= US patent 3 644 574) or in DE-OS 2 248 242 (= GB patent 1 409 275).

5 Particularly preferred graft polymers C are obtainable by a grafting reaction of

- $\alpha$  10 to 70, preferably 15 to 50, in particular 20 to 40 wt.%, relative to the graft polymer C, of at least one (meth)acrylic acid ester or 10 to 70, preferably 15 to 50, in particular 20 to 40 wt.% of a mixture of 10 to 50, preferably 20 to 10 35 wt.%, relative to the mixture, of acrylonitrile or (meth)acrylic acid esters and 50 to 90, preferably 65 to 80 wt.%, relative to the mixture, of styrene as the graft C.1 onto
- $\beta$  30 to 90, preferably 50 to 85, in particular 60 to 80 wt.%, relative to the graft polymer C, of a butadiene polymer having at least 50 wt.%, relative to  $\beta$ , of 15 butadiene residues as the grafting backbone C.2.

The gel content of the grafting backbone  $\beta$  is in general at least 20 wt.%, preferably 40 wt.% (measured in toluene), the degree of grafting G is 0.15 to 0.55 and the 20 average particle diameter  $d_{50}$  of the graft polymer C.2 is 0.05 to 2  $\mu\text{m}$ , preferably 0.1 to 0.6  $\mu\text{m}$ .

(Meth)acrylic acid esters  $\alpha$  are esters of acrylic acid or methacrylic acid with monohydric alcohols having 1 to 18 C atoms. Methacrylic acid methyl, ethyl and 25 propyl esters, n-butyl acrylate, t-butyl acrylate and t-butyl methacrylate are particularly preferred.

The grafting backbone  $\beta$  may contain, apart from butadiene residues, up to 50 wt.%, relative to  $\beta$ , of residues of other ethylenically unsaturated monomers, such as styrene, 30 acrylonitrile, esters of acrylic or methacrylic acid having 1 to 4 C atoms in the alcohol component (such as methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl

methacrylate), vinyl esters and/or vinyl ethers. The preferred grafting backbone  $\beta$  consists of pure polybutadiene.

5 The degree of grafting  $G$  denotes the weight ratio of grafted graft monomer to the grafting backbone and is dimensionless.

10 The average particle diameter  $d_{50}$  is the diameter both above and below which 50 wt.% of the particles lie. This value may be determined by ultracentrifuge measurements (W. Scholtan, H. Lange, *Kolloid-Z. und Z. Polymere* 250 (1972), 782-796).

Particularly preferred polymers  $C$  are, for example, also graft polymers prepared from

15  $\tau$  20 to 90 wt.%, relative to component  $C$ , of acrylate rubber having a glass transition temperature of  $<-20^{\circ}\text{C}$  as the grafting backbone  $C.2$  and

$\delta$  10 to 80 wt.%; relative to component  $C$ , of at least one polymerisable, ethylenically unsaturated monomer as the graft monomer  $C.1$ .

20 The acrylate rubbers  $\tau$  of the polymers  $C$  are preferably polymers prepared from acrylic acid alkyl esters, optionally having up to 40 wt.%, relative to  $\tau$ , of other polymerisable, ethylenically unsaturated monomers. Preferred polymerisable acrylic acid esters include  $C_1$ - $C_8$  alkyl esters, for example methyl, ethyl, butyl,  $n$ -octyl and 2-ethylhexyl esters; haloalkyl esters, preferably halo- $C_1$ - $C_8$ -alkyl esters, such as  
25 chloroethyl acrylate, as well as mixtures of these monomers.

Monomers having more than one polymerisable double bond may be copolymerised to achieve crosslinking. Preferred examples of crosslinking monomers are esters of unsaturated monocarboxylic acids having 3 to 8 C atoms and unsaturated monohydric  
30 alcohols having 3 to 12 C atoms or saturated polyols having 2 to 4 OH groups and 2 to 20 C atoms, such as for example ethylene glycol dimethacrylate, allyl methacrylate;

polyunsaturated heterocyclic compounds, such as for example trivinyl and triallyl cyanurate; polyfunctional vinyl compounds, such as di- and trivinylbenzenes; as well as triallyl phosphate and diallyl phthalate.

- 5 Preferred crosslinking monomers are allyl methacrylate, ethylene glycol dimethyl acrylate, diallyl phthalate and heterocyclic compounds comprising at least three ethylenically unsaturated groups.

10 Particularly preferred crosslinking monomers are the cyclic monomers triallyl cyanurate, triallyl isocyanurate, trivinyl cyanurate, triacryloylhexahydro-s-triazine, triallylbenzenes.

The quantity of the crosslinking monomers is preferably 0.02 to 5, in particular 0.05 to 2 wt.%, relative to the grafting backbone  $\tau$ .

15

In the case of cyclic crosslinking monomers having at least three ethylenically unsaturated groups, it is advantageous to restrict the quantity to below 1 wt.% of the grafting backbone  $\tau$ .

- 20 Preferred "other" polymerisable, ethylenically unsaturated monomers which, apart from the acrylic acid esters, may optionally be used in the production of the grafting backbone  $\tau$ , are, for example, acrylonitrile, styrene,  $\alpha$ -methylstyrene, acrylamides, vinyl C<sub>1</sub>-C<sub>6</sub>-alkyl ethers, methyl methacrylate, butadiene. Preferred acrylate rubbers as the grafting backbone  $\tau$  are emulsion polymers having a gel content of at least
- 25 60 wt.%.

Further suitable grafting backbones according to B.2 are silicone rubbers having active grafting sites, as are described in DE-OS 3 704 657, DE-OS 3 704 655, DE-OS 3 631 540 and DE-OS 3 631 539.

30

The gel content of the grafting backbone C.2 is determined in dimethylformamide at 25°C (M. Hoffmann, H. Krömer, R. Kuhn, *Polymeranalytik I & II*, Georg Thieme Verlag, Stuttgart, 1977).

- 5     The graft polymers C may be produced using known processes such as bulk, suspension, emulsion or bulk/suspension processes.

Since, as is known, the graft monomers are not necessarily completely grafted onto the grafting backbone during the grafting reaction, graft polymers C according to the  
10     invention are also taken to comprise those products which are obtained by polymerisation of the graft monomers in the presence of the grafting backbone.

The average particle diameter  $d_{50}$  is the diameter both above and below which 50 wt.% of the particles lie. This value may be determined by ultracentrifuge  
15     measurements (W. Scholtan, H. Lange, *Kolloid-Z. und Z. Polymere* 250 (1972), 782-796).

Thermoplastic vinyl copolymers are described below: Suitable vinyl (co)polymers D.1 are polymers of least one monomer from the group of vinyl aromatics, vinyl cyanides  
20     (unsaturated nitriles) (meth)acrylic acid ( $C_1$ - $C_8$ )-alkyl esters, unsaturated carboxylic acids as well as derivatives (such as anhydrides and imides) of unsaturated carboxylic acids. In particular, suitable (co)polymers comprise those prepared from

D.1.1   50 to 99, preferably 60 to 80 parts by weight of vinyl aromatics and/or ring-  
25     substituted vinyl aromatics, such as styrene,  $\alpha$ -methylstyrene, p-methylstyrene, p-chlorostyrene) and/or methacrylic acid ( $C_1$ - $C_8$ )-alkyl esters such as for example methyl methacrylate, ethyl methacrylate) and

D.1.2   1 to 50, preferably 20 to 40 parts by weight of vinyl cyanides (unsaturated  
30     nitriles) such as acrylonitrile and methacrylonitrile and/or (meth)acrylic ( $C_1$ - $C_8$ )-alkyl esters (such as for example methyl methacrylate, n-butyl acrylate,

t-butyl acrylate) and/or unsaturated carboxylic acids (such as maleic acid) and/or derivatives (such as anhydrides and imides) of unsaturated carboxylic acids (for example maleic anhydride and N-phenylmaleimide).

5 The (co)polymers D.1 are resinous, thermoplastic and rubber-free.

The copolymer prepared from D.1.1 styrene and D.1.2 acrylonitrile is particularly preferred.

10 The (co)polymers according to D.1 are known and may be produced by free-radical polymerisation, in particular by emulsion, suspension, solution or bulk polymerisation. The (co)polymers preferably have molecular weights  $\overline{M}_w$  (weight average, determined by light scattering or sedimentation) of between 15000 and 200000.

15 The thermoplastic vinyl (co)polymers D and the graft polymers C may be obtained as a mixture during the production thereof and be used as such in the process according to the invention.

20 Additives are described as follows: Conventional additives are, for example, fillers (for example mineral fillers), reinforcing materials (for example glass fibres), stabilisers (for example UV stabilisers, heat stabilisers, gamma radiation stabilisers), antistatic agents, flow auxiliaries, mould release agents, flame retardant additives, emulsifiers, nucleating agents, plasticisers, lubricants, dyes and pigments. The stated  
25 and further suitable additives are described, for example, in Gächter, Müller, *Kunststoff-Additive*, 3<sup>rd</sup> edition, Hanser Verlag, Munich, Vienna, 1989. The additives may be used alone or as a mixture, or in the form of masterbatches.

30 Fibrous or particulate fillers and reinforcing materials which may be added, and may also be surface-treated, are for example glass fibres, glass beads, glass textiles, glass mats, carbon fibres, aramid fibres, potassium titanate fibres, natural fibres, amorphous

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silica, magnesium carbonate, barium sulfate, feldspar, mica, silicates, quartz, talcum, kaolin, titanium dioxide, wollastonite and others. Preferred reinforcing materials are talcum and kaolin, particularly preferably glass fibres. The fillers and reinforcing materials may be provided with a suitable sizing system and a coupling agent or  
5 coupling agent system, for example based on silane.

Flame retardants which may be used individually or as a mixture are conventional commercial organic halogen compounds with synergists or conventional commercial organic nitrogen compounds or organic/inorganic phosphorus compounds. Mineral  
10 flame retardant additives such as magnesium hydroxides or hydrated Ca/Mg carbonates (for example DE-OS 4 236 122) may also be used. Halogenated, in particular brominated and chlorinated, compounds which may for example and preferably be mentioned are: 1,2-ethylenebistetrahydrophthalimide, epoxidised tetrabromobisphenol A resin, tetrabromobisphenol A oligocarbonate,  
15 tetrachlorobisphenol A oligocarbonate, pentabromopolyacrylate, brominated polystyrene. Suitable organic phosphorus compounds are the phosphorus compounds according to WO98/17720 (PCT/EP/05705), with triphenyl phosphate (TPP), resorcinol bis(diphenyl phosphate) including oligomers (RDP), as well as bisphenol A bisdiphenyl phosphate including oligomers (BDP), melamine phosphate, melamine  
20 pyrophosphate, melamine polyphosphate and the mixtures thereof. Nitrogen compounds which may in particular be considered are melamine and melamine cyanurate. Suitable synergists are, for example, antimony compounds, in particular antimony trioxide and antimony pentoxide, nanoscale minerals, such as for example barium sulfate, zinc compounds, tin compounds such as for example tin stannate and  
25 borates. Carbon formers and tetrafluoroethylene polymers may be added.

Stabilisers which may be used are, for example, sterically hindered phenols and/or phosphites, hydroquinones, aromatic secondary amines such as diphenylamines, substituted resorcinols, salicylates, benzotriazoles and benzophenones, as well as  
30 differently substituted representatives of these groups and mixtures thereof.

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Pigments which may be used are, for example, titanium dioxide, ultramarine blue, iron oxide, carbon black, phthalocyanines, quinacridones, perylenes, nigrosin and anthraquinones.

- 5 Nucleating agents which may be used are, for example, sodium phenylphosphinate, aluminium oxide, silicon dioxide and preferably talcum.

- 10 Lubricants and mould release agents which may be used are ester waxes, pentaerythritol tetrastearate (PETS), long-chain fatty acids (for example stearic acid or behenic acid), the salts thereof (for example Ca or Zn stearate) and amide derivatives (for example ethylene bisstearylamine) or montan waxes (mixtures of linear, saturated carboxylic acids having chain lengths of 28 to 32 C atoms) and low molecular weight polyethylene or polypropylene waxes.

- 15 Plasticisers which may be used are, for example, phthalic acid dioctyl ester, phthalic acid dibenzyl ester, phthalic acid butylbenzyl ester, hydrocarbon oils, N-(n-butyl)benzenesulfonamide.

- 20 The polymer melt produced using the described process is preferably used to produce pellets or semi-finished products, such as for example films, solid sheets, twin-wall sheets, profiles or tubes.

- 25 According to a preferred teaching of the invention, the product stream is conveyed by means of large-mouthed gear pumps, with all the product-conveying parts of the individual components being heated and those elements which come into contact with the product being lined with low-iron materials. Low-iron materials which are preferably used are Alloy 59 (2.4605), Inconel 686 (2.4606), Alloy-B2, Alloy C22, Alloy-C276, Alloy-C4, Alloy B2, Alloy B3 or Alloy B4.

- 30 Another development of the invention provides that a counter-rotating extruder or a co-rotating extruder is provided as the extruder for melting the blend components.

Particularly good results are achieved by a static mixer being provided as the mixer for mixing the components, in which case the ratio of mixing length  $L$  to mixing diameter  $D$  of the static mixer is preferably  $L:D = 14:1$ .

5 The invention is illustrated below in greater detail by a drawing which represents only one preferred practical Example, in which polycarbonate is drawn from primary production in a molten state.

10 The single Figure is a schematic representation of a direct compounding plant for a blend of polycarbonate, graft polymer, vinyl copolymer and additives (known as Bayblend®) or of polycarbonate, polybutylene terephthalate, graft polymer and additives (known as Pocan®).

15 In the practical Example, which is shown only schematically (Figure 1), a large-mouthed gear pump 2 conveys polycarbonate melt, which originates directly from a polycarbonate production plant 1, which is shown in no greater detail, through a static mixing section 3, through which a product side stream from an extruder 5, driven by a motor 4, for incorporating the blend components to be incorporated (graft polymers, vinyl copolymers and additives in the case of Bayblend®, or polybutylene  
20 terephthalate, graft polymers and additives in the case of Pocan®) is incorporated and through a die plate, which is shown in no greater detail, to a pelletiser 6.

25 Two or more extruders may also be used for melting the blend components to be incorporated. The blend components to be incorporated may also partially be incorporated directly into the melt stream between the mixing section 3 and the extruder 5. In the test rig, piping and discharge pumps were heated with heat-transfer oil; the piping being made from Inconel 686.

30 The analytical values of the polymer blend produced with the stated plant (quantity produced approx. 10 tonnes) are within the desired specification of corresponding blends produced in the conventional manner. In particular in the case of Pocan®, the



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mechanical properties, in particular the low temperature toughness, of the resultant moulding compositions completely match those of the corresponding polymer blend produced in the conventional manner.

- 5 The volumetric flow rates were 330 kg/h of polycarbonate melt, into which 140 kg/h of blend components to be incorporated in the case of Bayblend® and 83 kg/h of polymer components to be incorporated in the case of Pocan® were incorporated online by means of the static mixing section 3. The polymer blends produced using the plant according to the invention exhibit a residual monochlorobenzene content of  
10 480 ppm.

**Patent Claims**

1. Process for the production of a thermoplastic polymer blend from polycarbonate, a thermoplastic polyester and/or vinyl polymers, optionally together with further additives, characterised by the following steps:
- 5
- drawing at least one of the thermoplastics used for the production of the polymer blend in the molten state directly from primary production,
  - optionally melting the blend components which are to be incorporated,
  - 10 - adding the blend components which are to be incorporated into the polymer melt drawn from primary production,
  - mixing all the components in a mixing section and
  - cooling and optionally pelletising the polymer melt.
- 15 2. Process according to claim 1, characterised in that the thermoplastic polyester used comprises polyalkylene terephthalates, preferably polybutylene terephthalate, polytrimethylene terephthalate and/or polyethylene terephthalate, particularly preferably polybutylene terephthalate (PBT).
- 20 3. Process according to claim 1 or 2, characterised in that the thermoplastic which is drawn in the molten state directly from primary production comprises thermoplastic polyesters, preferably polybutylene terephthalate, polytrimethylene terephthalate or polyethylene terephthalate, particularly preferably polybutylene terephthalate.
- 25 4. Process according to claim 1 or 2, characterised in that the thermoplastic which is drawn in the molten state from primary production is aromatic polycarbonate.

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5. Process according to claim 4, characterised in that the temperature of the molten polycarbonate is 260 to 320°C, preferably 270 to 300°C, particularly preferably 280 to 290°C.
- 5      6. Process according to any one of claims 2 to 5, characterised in that polybutylene terephthalate is drawn in the molten state from primary production and the temperature of the molten polybutylene terephthalate is 220 to 320°C, preferably 230 to 300°C, particularly preferably 240 to 280°C.
- 10      7. Process according to any one of claims 1 to 6, characterised in that thermoplastic moulding compositions are produced which contain
- 15      A: 2 to 98 parts by weight of thermoplastic polyester, particularly preferably 30 to 50 parts by weight of thermoplastic polyester, preferably in total 10 to 60 parts by weight of polybutylene terephthalate, polytrimethylene terephthalate and/or polyethylene terephthalate, particularly preferably 10 to 60 parts by weight of polybutylene terephthalate,
- 20      B: 2 to 98 parts by weight of aromatic polycarbonate, preferably 40 to 90 parts by weight of aromatic polycarbonate,
- 25      C: 0 to 30 parts by weight of graft polymer, preferably 4 to 25 parts by weight of graft polymer,
- 30      D: 0 to 25 parts by weight of additives, preferably 0.05 to 20 parts by weight of additives, particularly preferably 0.1 to 10 parts by weight of additives,
- wherein the sum of all parts by weight of components A-D is 100.

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8. Process according to any one of claims 1 to 6, characterised in that thermoplastic moulding compositions are produced which contain

5

A: 2 to 98 parts by weight of thermoplastic polyester, preferably in total 10 to 60 parts by weight of polybutylene terephthalate, polytrimethylene terephthalate and/or polyethylene terephthalate, particularly preferably 10 to 60 parts by weight of polybutylene terephthalate,

10

B: 2 to 98 parts by weight of aromatic polycarbonate, preferably 40 to 90 parts by weight of aromatic polycarbonate,

C: 0 to 30 parts by weight of graft polymer, preferably 4 to 25 parts by weight of graft polymer,

15

D: 0 to 30 parts by weight of thermoplastic vinyl copolymer, preferably 4 to 25 parts by weight of thermoplastic vinyl copolymer,

20

E: 0 to 25 parts by weight of additives, preferably 0.05 to 20 parts by weight of additives, particularly preferably 0.1 to 10 parts by weight of additives,

wherein the sum of all parts by weight of components A-E is 100.

25

9. Process according to any one of claims 1 to 6, characterised in that thermoplastic moulding compositions are produced which contain

A: 40 to 99 parts by weight of aromatic polycarbonate, preferably 60 to 98 parts by weight of aromatic polycarbonate,

- B: 0 to 60 parts by weight of graft polymer, preferably 1 to 40 parts by weight of graft polymer, particularly preferably 2 to 25 parts by weight of graft polymer
- 5 C: 0 to 45 parts by weight of thermoplastic vinyl copolymer, preferably 0 to 30 parts by weight of thermoplastic vinyl copolymer, particularly preferably 2 to 25 parts by weight of thermoplastic vinyl copolymer,
- 10 D: 0 to 30 parts by weight of additives, preferably 0.05 to 25 parts by weight of additives, particularly preferably 0.1 to 17 parts by weight of additives,

wherein the sum of all parts by weight of components A-D is 100.

- 15 10. Process according to any one of claims 1 to 9, characterised in that the blend components which are to be incorporated are partially or completely physically premixed in solid form.
- 20 11. Process according to any one of claims 1 to 10, characterised in that the blend components which are to be incorporated are partially or completely used as a masterbatch, *i.e.* they have previously been mixed as a melt.
- 25 12. Apparatus for the continuous production of a thermoplastic polymer blend from polycarbonate and a thermoplastic polymer and/or vinyl polymer optionally together with further additives, substantially consisting of a plant (1) for the production of polycarbonate, wherein the polycarbonate melt is drawn directly from this plant and at least one extruder (5) for melting the blend components, a mixer (3) and an apparatus for pelletising the polymer blend, wherein the individual components are interconnected by piping.

13. Apparatus according to claim 12, characterised in that large-mouthed gear pumps (2) are provided for conveying the product stream.
- 5 14. Apparatus according to claim 12 or 13, characterised in that the product-conveying parts of all components are heated.
- 10 15. Apparatus according to any one of claims 12 to 14, characterised in that the elements which come into contact with the product stream consist of a low-iron material.
16. Apparatus according to claim 15, characterised in that the low-iron material is selected from the range: Alloy 59 (2.4605), Inconell 686 (2.4606), Alloy-B2, Alloy C22, Alloy-C276, Alloy-C4, Alloy B2, Alloy B3, Alloy B4.
- 15 17. Apparatus according to claim 16, characterised in that the low-iron material consists of Alloy 59 (2.4605).
- 20 18. Apparatus according to any one of claims 12 to 17, characterised in that a counter-rotating extruder is provided as the extruder (5) for melting the blend components.
- 25 19. Apparatus according to any one of claims 12 to 17, characterised in that a co-rotating extruder is provided as the extruder (5) for melting the blend components.
20. Apparatus according to any one of claims 12 to 19, characterised in that a static mixer is provided as the mixer (3) for mixing the blend components.
- 30 21. Apparatus according to claim 20, characterised in that the ratio of mixing length L to mixing diameter D of the mixer (3) L:D is 14:1.

22. Use of the polymer melt produced using the process of any one of claims 1 to 11 for the production of semi-finished products.